NASA CR-57010
(GCA Tech. Rep. No. 64-5-N)

N64-27381
Code-1 Cat. 23

31p

PLANETARY PHYSICS

IV: AN EXPANSION METHOD FOR CALCULATING ATOMIC PROPERTIES

I. THE ^2S AND $^2P^0$ STATES OF THE LITHIUM SEQUENCE

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OTS PRICE

XEROX $ 3.60 ph

MICROFILM $

Prepared under Contract No. NASw-840 by
GEOPHYSICS CORPORATION OF AMERICA
Bedford, Mass.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

ABSTRACT

27381

An expansion method is used to calculate the expectation values of various operators for the lowest ^2S and $^2P^0$ states of all members of the lithium sequence. The method is extended to the calculation of matrix elements connecting the two states and the electric dipole transition integrals are calculated. A comparison with the results of more refined calculations shows that despite its simplicity the method is capable of high accuracy.

Author:

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AN EXPANSION METHOD FOR CALCULATING ATOMIC PROPERTIES

I. THE ^2S AND $^2P^o$ STATES OF THE LITHIUM SEQUENCE

M. Cohen and A. Dalgarno

1. INTRODUCTION

An expansion method has been used to calculate the expectation values of various operators for the ground states of all members of the helium and the beryllium isoelectronic sequences (Cohen & Dalgarno 1961). It may also be applied to excited states and to the calculation of matrix elements between different states.

2. THE RESTRICTED HARTREE-FOCK APPROXIMATION

2.1. The $1s^2 2s\ ^2S$ configuration

We choose a set of units in which the scale of distance is Z a.u. and of energy is Z^2 a.u., where Z is the nuclear charge. Then with the definitions

$$H_k = \frac{1}{2}\left\{\nabla_r^2 - \frac{k(k+1)}{r^2}\right\} - \frac{1}{r} \tag{1}$$

and

$$Y^k\ (u,v) = \frac{1}{r^{k+1}}\int_0^r u(s).v(s)s^{k+2}ds + r^k\int_r^\infty \frac{u(s).v(s)}{s^{k-1}}\,ds, \tag{2}$$

the restricted Hartree-Fock equations for the radial 1s and 2s-orbitals u(r) and v(r) are

$$H_0u + [Y^0(1s,1s)+Y^0(2s,2s)]u - \frac{1}{2}Y^0(1s,2s)v = \epsilon(1s)u + \frac{1}{2}\epsilon\ (1s,2s)v \tag{3}$$

and

$$H_0v + 2Y^0\ (1s,1s)v - Y^0(1s,2s)u = \epsilon(2s)\ v+\epsilon(1s,2s)u. \tag{4}$$

With orthonormal u and v, it follows that

$$\epsilon(1s) = \langle u|H_0|u\rangle + \langle u|Y^0(1s,1s) + Y^0(2s,2s)|u\rangle - \frac{1}{2}\ \langle u|Y^0(1s,2s)|v\rangle, \tag{5}$$

$$\epsilon(2s) = \langle v|H_0|v\rangle + 2\ \langle v|Y^0(1s,1s)|v\rangle - \langle v|Y^0(1s,2s)|u\rangle\ , \tag{6}$$

and

$$\epsilon(1s,2s) = -\ \langle v|Y^0(2s,2s)|u\rangle = -\langle v|Y^0(1s,2s)|v\rangle\ . \tag{7}$$

Expanding in powers of Z^{-1},

$$\left.\begin{aligned} u &= u_0 + u_1 + \ldots, \quad v = v_0 + v_1 + \ldots, \\ \epsilon(n\ell) &= \epsilon_0(n\ell) + \epsilon_1(n\ell) + \ldots, \end{aligned}\right\} \tag{8}$$

it follows that

$$Y^k(n\ell,n'\ell') = Y_1^k(n\ell,n'\ell') + Y_2^k(n\ell,n'\ell') + \ldots$$

and

$$\epsilon(n\ell,n'\ell') = \epsilon_1(n\ell,n'\ell') + \epsilon_2(n\ell,n'\ell') + \ldots. \tag{9}$$

The zero-order equations derived from (3) and (4) are

$$(H_0 - \epsilon_0(1s))\, u_0 = 0$$

and

$$(H_0 - \epsilon_0(2s))\, v_0 = 0, \tag{10}$$

which have the orthonormal hydrogenic solutions

$$\left.\begin{aligned} u_0 &= 2 \exp(-r), & \epsilon_0(1s) &= -\tfrac{1}{2}, \\ v_0 &= (1/2\sqrt{2})\,(2 - r)\exp(-\tfrac{1}{2}r), & \epsilon_0(2s) &= -\tfrac{1}{8}\,. \end{aligned}\right\} \tag{11}$$

From the first-order equations,

$$(H_0-\epsilon_0(1s))u_1+[Y_1^0(1s,1s)+Y_1^0(2s,2s) - \epsilon_1(1s)]u_0 = \tfrac{1}{2}[Y_1^0(1s,2s)+\epsilon_1(1s,2s)]v_0 \tag{12}$$

and

$$(H_0-\epsilon_0(2s))v_1+[2Y_1^0(1s,1s)-\epsilon_1(2s)]v_0=[Y_1^0(1s,2s)+\epsilon_1(1s,2s)]u_0, \tag{13}$$

we have that

$$\epsilon_1(1s) = \left\langle u_0 \middle| Y_1^0(1s,1s) \middle| u_0 \right\rangle + \left\langle u_0 \middle| Y_1^0(2s,2s) \middle| u_0 \right\rangle - \tfrac{1}{2} \left\langle u_0 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle , \tag{14}$$

$$\epsilon_1(2s) = 2 \left\langle u_0 \middle| Y_1^0(1s,1s) \middle| v_0 \right\rangle - \left\langle v_0 \middle| Y_1^0(1s,2s) \middle| u_o \right\rangle \tag{15}$$

and

$$\epsilon_1(1s,2s) = - \left\langle v_0 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle . \tag{16}$$

The Slater integrals appearing in (14), (15) and (16) are gathered together for convenient reference in appendix I. Similarly, from the second-order equations we have that

$$\epsilon_2(1s) = 3 \left\langle u_1 \middle| Y_1^0(1s,1s) \middle| u_0 \right\rangle + 2 \left\langle v_1 \middle| Y_1^0(1s,2s) \middle| v_o \right\rangle + \left\langle u_1 \middle| Y_1^0(2s,2s) \middle| u_0 \right\rangle$$
$$- \left\langle v_1 \middle| Y_1^0(1s,2s) \middle| u_0 \right\rangle - \tfrac{1}{2} \left\langle u_1 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle - \tfrac{1}{2} \left\langle v_1 \middle| u_0 \right\rangle \epsilon_1(1s,2s) \tag{17}$$

and

$$\epsilon_2(2s) = 2 \left\langle v_1 \middle| Y_1^0(1s,1s) \middle| v_0 \right\rangle + 4 \left\langle u_1 \middle| Y_1^0(2s,2s) \middle| u_0 \right\rangle - 2 \left\langle u_1 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle$$
$$- \left\langle v_1 \middle| Y_1^0(1s,2s) \middle| u_0 \right\rangle - \left\langle u_1 \middle| v_0 \right\rangle \epsilon_1(1s,2s), \tag{18}$$

where we have taken u and v normalized up to first order, so that

$$\left\langle u_1 \middle| u_0 \right\rangle = \left\langle v_1 \middle| v_0 \right\rangle = 0. \tag{19}$$

If the total energy E is similarly expanded,

$$E = E_0 + E_1 + \ldots , \tag{20}$$

it may be shown that

$$2\epsilon_n(1s) + \epsilon_n(2s) = (n+1)E_n; \tag{21}$$

the matrix elements appearing in (17) and (18) have been evaluated by Linderberg (1961) and lead finally to the energy expansion (in conventional atomic units)

$$E = -1.125Z^2 + 1.022\ 805\ 21Z - 0.354\ 549\ 03 + O(Z^{-1}). \tag{22}$$

The expectation value $\langle L$ of an operator

$$L = \ell(r_1) + \ell(r_2) + \ell(r_3) \tag{23}$$

is given in the restricted Hartree-Fock approximation by

$$\left.\begin{aligned}\langle L\rangle &= 2\langle u|\ell|u\rangle + \langle v|\ell|v\rangle\\ &= 2\langle \ell|1s\rangle + \langle \ell|2s\rangle\ \text{, say.}\end{aligned}\right\} \tag{24}$$

The zero-order contribution is

$$\left.\begin{aligned}\langle L\rangle_0 &= 2\langle \ell|1s\rangle_0 + \langle \ell|2s\rangle_0\\ &= 2\langle u_0|\ell|u_0\rangle + \langle v_0|\ell|v_0\rangle\end{aligned}\right\} \tag{25}$$

and the first-order contribution is

$$\left.\begin{aligned}\langle L\rangle_1 &= 2\langle \ell|1s\rangle_1 + \langle \ell|2s\rangle_1\\ &= 4\langle u_1|\ell|u_0\rangle + 2\langle v_1|\ell|v_0\rangle,\end{aligned}\right\} \tag{26}$$

on account of (19).

Following the procedures of Dalgarno & Stewart (1956, 1958) we introduce the functions x and y which satisfy

$$(H_0 - \epsilon_0(1s))\ x + (\ell - \langle \ell | 1s \rangle_0)\ u_0 = 0, \tag{27}$$

$$(H_0 - \epsilon_0(2s))\ y + (\ell - \langle \ell | 2s \rangle_0)\ v_0 = 0 \tag{28}$$

and

$$\langle x | u_0 \rangle = \langle y | v_0 \rangle = 0 \tag{29}$$

We note that it follows from (10), (27) and (28) that

$$\langle x | v_0 \rangle + \langle y | u_0 \rangle = 0. \tag{30}$$

We now have (from (12), (13), (19), (27) to (29))

$$\langle \ell | 1s \rangle_1 = 2 \langle u_1 | \ell | u_0 \rangle = 2\Big\{ \langle x | Y_1^0(1s,1s) | u_0 \rangle + \langle x | Y_1^0(2s,2s) | u_0 \rangle - \tfrac{1}{2} \langle x | Y_1^0(1s,2s) | v_0 \rangle - \tfrac{1}{2} \epsilon_1(1s,2s) \langle x | v_0 \rangle \Big\} \tag{31}$$

and

$$\langle \ell | 2s \rangle_1 = 2 \langle v_1 | \ell | v_0 \rangle = 2\Big\{ 2 \langle y | Y_1^0(1s,1s) | v_0 \rangle - \langle y | Y_1^0(1s,2s) | u_0 \rangle - \epsilon_1(1s,2s) \langle y | u_0 \rangle \Big\} \tag{32}$$

so that

$$\langle L \rangle_1 = 2\Big\{ 2 \langle x | Y_1^0(1s,1s) | u_0 \rangle + 2 \langle x | Y_1^0(2s,2s) u_0 \rangle + 2 \langle y | Y_1^0(1s,1s) | v_0 \rangle - \langle x | Y_1^0(1s,2s) | v_0 \rangle - \langle y | Y_1^0(1s,2s) | u_0 \rangle \Big\} \tag{33}$$

which is independent of the non-diagonal Lagrange multiplier $\epsilon_1(1s,2s)$.

The solutions of (27) and (28) for $\ell = r^n (n > 1)$, $r^{-1} r^{-2}$, $\delta(\mathbf{r})$ and ∇^4 have been listed by Cohen & Dalgrano (1961). Using them, we can write the expectation values of these operators in atomic units (correct to first order in Z^{-1}) in the form

$$\langle \ell | 1s \rangle = A(1s)\{Z - \sigma(1s)\}^n, \tag{34}$$

$$\langle \ell | 2s \rangle = A(2s)\{Z - \sigma(2s)\}^n \tag{35}$$

(Dalgarno & Stewart 1960; Cohen & Dalgarno 1961) and we present in Tables 1 and 2 the values of the constants A, σ and n. It is of interest to examine the influence of the direct and exchange interactions on the effective screening constants $\sigma(1s)$ and $\sigma(2s)$ and the tables show the values obtained by including successively in the evaluation of (33) and (34) the direct interaction, the exchange interaction and the Lagrange multiplier terms.

The effects of the Lagrange multiplier terms are small and the behavior of the screening constants is very similar to that found in the Hartree-Fock approximation for the beryllium sequence.

TABLE 1. CONSTANTS FOR THE 1s SHELL CONTRIBUTIONS TO EXPECTATION VALUES (^2S STATE)

			σ(1s)			
operator ℓ	n	A(1s)	(a)	(b)	(c)	(d)
r^2	-2	3	0.3984	0.4352	0.4146	0.4260
r	-1	$\frac{3}{2}$	0.3750	0.4093	0.3890	0.3975
r^{-1}	1	1	0.3125	0.3413	0.3230	0.3278
r^{-2}	2	2	0.2713	0.2967	0.2803	0.2839
$\pi\delta(\mathbf{r})$	3	1	0.2225	0.2435	0.2299	0.2326
$\nabla 4$	4	5	0.2046	0.2240	0.2113	0.2136

(a) 1s-1s interaction only.

(b) 1s-1s interaction and direct 1s-2s interaction.

(c) 1s-1s interaction and direct exchange 1s-2s interactions.

(d) (c) with the addition of the Lagrange multiplier term.

TABLE 2. CONSTANTS FOR THE 2s SHELL CONTRIBUTIONS TO EXPECTATION VALUES

operator ℓ	n	A(2s)	$\sigma(2s)$ (a)	$\sigma(2s)$ (b)	$\sigma(2s)$ (c)
r^2	-2	42	1.3865	1.2350	1.2333
r	-1	6	1.3827	1.2429	1.2386
r^{-1}	1	$\frac{1}{4}$	1.4484	1.5068	1.4684
r^{-2}	2	$\frac{1}{4}$	1.2700	1.4576	1.3980
$\pi\delta(\mathbf{r})$	3	$\frac{1}{8}$	0.9784	1.1035	1.0603
$\nabla 4$	4	$\frac{13}{16}$	0.9132	0.9431	0.9151

(a) Direct 1s-2s interaction only.

(b) Direct and exchange 1s-2s interactions.

(c) (b) with the addition of the Lagrange multiplier term.

2.2. The $1s^2 2p\ ^2P^0$ configuration

The restricted Hartree-Fock equations for the radial 1s- and 2p-orbitals u'(r) and w(r) are

$$H_0u' + [Y^0(1s',1s') + Y^0(2S,2p)]u' - \tfrac{1}{6}Y'(1s',2p)w = \epsilon'(1s)u' \tag{36}$$

and
$$H_1w + 2Y^0(1s',1s')w - \tfrac{1}{3}Y^1(1s',2p)u' = \epsilon(2p)w, \tag{37}$$

and with normalized u' and w, we have that

$$\epsilon'(1s) = \left\langle u'\middle|H_0\middle|u'\right\rangle + \left\langle u'\middle|Y^0(1s',1s') + Y^0(2p,2p)\middle|u'\right\rangle - \tfrac{1}{6}\left\langle u'\middle|Y^1(1s',2p)\middle|w\right\rangle \tag{38}$$

and
$$\epsilon(2p) = \left\langle w\middle|H_1\middle|w\right\rangle + 2\left\langle w\middle|Y^0(1s',1s')\middle|w\right\rangle - \tfrac{1}{3}\left\langle w\middle|Y^1(1s',2p)\middle|u'\right\rangle . \tag{39}$$

Expanding as before, the zero-order equations derived from (36) and (37) are

$$\left.\begin{aligned} &(H_0 - \epsilon_0'(1s))\ u_0' = 0 \\ \text{and}\quad &(H_1 - \epsilon_0(2p))\ w_0 = 0, \end{aligned}\right\} \tag{40}$$

which have the hydrogenic solutions

$$\left.\begin{aligned} u_0' &= 2\exp(-r), & \epsilon_0'(1s) &= -\tfrac{1}{2}, \\ w_0 &= (1/2\sqrt{2})r\ \exp(-\tfrac{1}{2}r), & \epsilon_0(2p) &= -\tfrac{1}{8}. \end{aligned}\right\} \tag{41}$$

We may therefore write u_0 and $\epsilon_0(1s)$ for the zero-order terms in both the ^2S and $^2P^0$ configurations, and the single kernel function $Y_1^0(1s',1s') = Y_1^0(1s,1s)$. Then, from the first order equations

$$(H_0-\epsilon_0(1s))u_1' + [Y_1^0(1s,1s) + Y_1^0(2p,2p)-\epsilon_1'(1s)]u_0 = \tfrac{1}{6}Y_1^1(1s,2p)w_0 \tag{42}$$

and $$(H_1-\epsilon_0(2p))w_1 + [2Y_1^0(1s,1s)-\epsilon_1(2p)]w_0 = \tfrac{1}{3}Y_1^1(1s,2p)u_0, \tag{43}$$

we have that

$$\epsilon_1'(1s) = \left\langle u_0\middle|Y_1^0(1s,1s)\middle|u_0\right\rangle + \left\langle u_0\middle|Y_1^0(2p,2p)\middle|u_0\right\rangle -\frac{1}{6}\left\langle u_0\middle|Y_1^1(1s,2p)\middle|w_0\right\rangle \tag{44}$$

and $$\epsilon_1(2p) = 2\left\langle w_0\middle|Y_1^0(1s,1s)\middle|w_0\right\rangle -\frac{1}{3}\left\langle w_0\middle|Y_1^1(1s,2p)\middle|u_0\right\rangle ; \tag{45}$$

values of these Slater integrals are listed in appendix I, and the total energy is given in atomic units by

$$E = -1.125Z^2 + 1.093\ 526\ 14Z + \ldots . \tag{46}$$

To evaluate the matrix elements $\langle L\rangle$ for the $^2P^0$ state, we introduce the function z which satisfies

$$(H_1-\epsilon_0(2p))z + (\ell- \langle \ell|2p\rangle_0)w_0 = 0 \tag{47}$$

and $$\langle z|w_0\rangle = 0. \tag{48}$$

Then we have in complete analogy with (31) and (32)

$$\langle \ell|1s'\rangle_1 = 2\langle u_1'|\ell|u_0\rangle = 2\left\{\left\langle x\middle|Y_1^0(1s,1s)\middle|u_0\right\rangle + \left\langle x\middle|Y_1^0(2p,2p)\middle|u_0\right\rangle -\frac{1}{6}\left\langle x\middle|Y_1^1(1s,2p)\middle|w_0\right\rangle\right\} \tag{49}$$

and $$\langle \ell|2p\rangle_1 = 2\langle w_1|\ell|w_0\rangle = 2\left\{2\left\langle z\middle|Y_1^0(1s,1s)\middle|w_0\right\rangle -\frac{1}{3}\left\langle z\middle|Y_1^1(1s,2p)\middle|u_0\right\rangle\right\} \tag{50}$$

We have solved (47) for various operators ℓ. For $\ell = r^n (n \geqslant 1)$,

$$\langle \ell | 2p \rangle_0 = (n+4)!/24 \tag{51}$$

and

$$z = -2(n+4)! \sum_{k=2}^{n+1} \frac{r^k w_0}{k(k+3)!} ; \tag{52}$$

for $\ell = r^{-1}$,

$$\langle \ell | 2p \rangle_0 = \frac{1}{4} \tag{53}$$

and

$$z = \frac{1}{2} r w_0 \tag{54}$$

and for $\ell = r^{-2}$,

$$\langle \ell | 2p \rangle_0 = \frac{1}{12} \tag{55}$$

and

$$z = (\frac{1}{6} r + \frac{2}{3} \ln r) w_0 . \tag{56}$$

For $\ell = r^{-3}$, (47) has strictly no well-behaved solution. The difficulty may be circumvented by considering instead the operator $\ell = r^{-3} + 2\pi\delta(\mathbf{r})$ and noting that

$$\langle w | \delta(\mathbf{r}) | w \rangle = 0 \tag{57}$$

to all orders. Corresponding to $\ell = r^{-3} + 2\pi\delta(\mathbf{r})$,

$$\langle \ell | 2p \rangle_0 = \frac{1}{24} \tag{58}$$

and

$$z = (-1/r + \frac{1}{3} \ln r + \frac{1}{12} r) w_0 . \tag{59}$$

Similarly we replace r^{-4} and obtain

$$\langle \ell | 2p \rangle_0 = \frac{1}{24} \tag{60}$$

and

$$z = (-1/r^2 - 1/r + \frac{1}{3} \ln r + \frac{1}{12} r) w_0 . \tag{61}$$

The operator ∇^4 presents no difficulty, and we find

$$\left\langle \ell | 2p \right\rangle_0 = \frac{7}{48} \tag{62}$$

and

$$z = (-4/r + \frac{8}{3}\ln r + \frac{1}{6}r)w_0. \tag{63}$$

The expectation values of these operators may now be written in <u>atomic units</u> (correct to first order in Z^{-1}) in the form

$$\left\langle \ell | 1s' \right\rangle = A'(1s)[Z - \sigma(1s)]^n \tag{64}$$

and

$$\left\langle \ell | 2p \right\rangle = A(2p)[Z - \sigma(2p)]^n \tag{65}$$

as for the ^2S state. The values of n, A and σ obtained by successively including the direct and exchange interaction terms are given in Tables 3 and 4.

The screening constants for the 1s shell of the $^2P^0$ state are similar to but slightly larger than those of the ^2S state, the increased screening arising from the exchange interaction with the outer shell which decreases the screening in the ^2S state and increases it in the $^2P^0$ state. The screening constants of the outer electron in the $^2P^0$ state are markedly larger than those in the ^2S state and in contrast to those in the ^2S state they increase uniformly with increasing distance from the nucleus. The anomalous behaviour of the ^2S screening constants has been attributed previously to the node of the 2s orbital (Cohen & Dalgarno 1961).

In the case of the $^2P^0$ state, the screening constants of the outer electrons are large and the screening approximation may be misleading for the lowest number of the sequence (Z=3) but it should be reliable for the higher numbers.

TABLE 3. CONSTANTS FOR THE 1s SHELL CONTRIBUTIONS TO EXPECTATION VALUES ($^2P^0$ STATE)

operator ℓ	n	$A'(1s)$	$\sigma'(1s)$ (a)	$\sigma'(1s)$ (b)	$\sigma'(1s)$ (c)
r^2	-2	3	0.3984	0.4304	0.4542
r	-1	$\frac{3}{2}$	0.3750	0.4020	0.4223
r^{-1}	1	1	0.3125	0.3303	0.3445
r^{-2}	2	2	0.2713	0.2853	0.2968
$\pi\delta(\mathbf{r})$	3	1	0.2225	0.2439	0.2529
∇^4	4	5	0.2046	0.2231	0.2310

(a) 1s-1s interaction only.

(b) 1s-1s interaction and direct 1s-2p interaction.

(c) 1s-1s interaction and direct exchanges 1s-2p interactions.

TABLE 4. CONSTANTS FOR THE 2p SHELL CONTRIBUTIONS TO EXPECTATION VALUES

operator ℓ	n	A(2p)	$\sigma(2p)$ (a)	$\sigma(2p)$ (b)
r^2	-2	30	1.8566	1.7053
r	-1	5	1.8436	1.6836
r^{-1}	1	$\frac{1}{4}$	1.7996	1.6176
r^{-2}	2	$\frac{1}{12}$	1.7610	1.5660
$r^{-3}+2\pi\delta(\mathbf{r})$	3	$\frac{1}{24}$	1.7008	1.4928
$\left.\begin{array}{l} r^{-4}+2\pi\delta(\mathbf{r}) \\ +(4\pi/r)\delta(\mathbf{r}) \end{array}\right\}$	4	$\frac{1}{24}$	1.6050	1.3884
∇^4	4	$\frac{7}{48}$	1.6927	1.4806

(a) Direct 2p-1s interaction.

(b) Direct and exchange 2p-1s interaction.

2.3. $1s^2 2s\,{}^2S - 1s^2 2p\,{}^2P^0$ transitions

The procedure by which we are able to avoid the determination of the first-order orbitals may be extended to the calculation of matrix elements connecting different states. To first order

$$\langle v|\ell|w\rangle = \langle v|\ell|w\rangle_0 + \langle v|\ell|w\rangle_1, \tag{66}$$

where

$$\langle v|\ell|w\rangle_0 = \langle v_0|\ell|w_0\rangle \tag{67}$$

and

$$\langle v|\ell|w\rangle_1 = \langle v_1|\ell|w_0\rangle + \langle v_0|\ell|w_1\rangle, \tag{68}$$

assuming that

$$\langle v_1|v_0\rangle = \langle w_1|w_0\rangle = 0. \tag{69}$$

We now introduce functions V and W such that

$$(H_0 - \epsilon_0(2s))V + \ell w_0 - \langle v_0|\ell|w_0\rangle\, v_0 = 0, \tag{70}$$

$$(H_1 - \epsilon_0(2p))W + \ell v_0 - \langle v_0|\ell|w_0\rangle\, w_0 = 0 \tag{71}$$

and

$$\langle V|v_0\rangle = \langle W|w_0\rangle = 0. \tag{72}$$

It then follows from (13), (43), (69) to (72) that

$$\langle v|\ell|w\rangle_1 = [2\langle V|Y_1^0(1s,1s)|v_0\rangle - \langle V|Y_1^0(1s,2s)|u_0\rangle - \epsilon_1(1s,2s)\langle V|u_0\rangle]$$
$$+[2\langle W|Y_1^0(1s,1s)|w_0\rangle - \tfrac{1}{3}\langle W|Y_1^1(1s,2p)|u_0\rangle]. \tag{73}$$

The calculation of electric dipole transition probabilities, using the dipole length formulation, may be reduced to the evaluation of

$$R^2 = \tfrac{1}{3}|\langle v|r|w\rangle|^2. \tag{74}$$

To zero order, $$\langle v_0|r|w_0\rangle = -3\sqrt{3}|Z, \tag{75}$$

and the solutions of (70) and (71) for this case are

$$V = (1/2\sqrt{6})(6r^2-r^3)\exp(-\tfrac{1}{2}r) \tag{76}$$

and $$W = (1/2\sqrt{2})r^3\exp(-\tfrac{1}{2}r); \tag{77}$$

thus, correct to first order

$$\langle v|r|w\rangle = -\frac{3\sqrt{3}}{Z}\left\{1 + \frac{1.698\ 664}{Z} + O(Z^{-2})\right\} \tag{78}$$

and applying the screening approximation,

$$R^2 = 9/(Z - 1.699)^2. \tag{79}$$

A comparison of the values of R^2 given by (79) with the results of more refined variational calculations by Flannery & Stewart (1963) is made in Table 5. Equation (79) is correct in the limit of infinite Z but even for Z as low as 3 the error does not exceed 4%. Since the convergence of (78) is poor for Z=3, the smallness of the error of (79) may be partly fortuitous.

TABLE 5. VALUES OF R FOR THE $^2S-^2P^0$ TRANSITION

Z	Flannery & Stewart	equation (79)
3	2.3820	2.3059
4	1.3207	1.3038
5	0.9129	0.9088
6	0.6981	0.6975
7	0.5653	0.5659
8	0.4752	0.4761

3. THE UNRESTRICTED HARTREE-FOCK APPROXIMATION

3.1. The (1s 1s' 2s) configuration

The unrestricted Hartree-Fock equations for the radial 1s, 1s' and 2s orbitals $u'(r)$, $u^{\ddagger}(r)$ and $v^{\dagger}(r)$ are

$$H_0u^{\dagger} + \left[Y^0(1s^{\ddagger},1s^{\ddagger})+Y^0(2s^{\dagger},2s^{\dagger})\right]u^{\dagger} - Y^0(1s^{\dagger},2s^{\dagger})v^{\dagger} = \epsilon(1s^{\dagger})u^{\dagger}, \tag{80}$$

$$H_0u^{\ddagger} + \left[Y^0(1s^{\dagger},1s^{\dagger})+Y^0(2s^{\dagger},2s^{\dagger})\right]u^{\ddagger} = \epsilon(1s^{\ddagger})u^{\ddagger}, \tag{81}$$

$$H_0v^{\dagger} + \left[Y^0(1s^{\dagger},1s^{\dagger})+Y^0(1s^{\ddagger},1s^{\ddagger})\right]v^{\dagger} - Y^0(1s^{\dagger},2s^{\dagger})u^{\dagger} = \epsilon(2s^{\dagger})v^{\dagger}, \tag{82}$$

where the orbitals $u^{\dagger}$ and $v^{\dagger}$ are associated with parallel spins. Then

$$\epsilon(1s^{\dagger})=\langle u^{\dagger}|H_0|u^{\dagger}\rangle+\langle u^{\dagger}|Y^0(1s^{\ddagger},1s^{\ddagger})+Y^0(2s^{\dagger},2s^{\dagger})|u^{\dagger}\rangle-\langle u^{\dagger}|Y^0(1s^{\dagger},2s^{\dagger})|v^{\dagger}\rangle \tag{83}$$

$$\epsilon(1s^{\ddagger})=\langle u^{\ddagger}|H_0|u^{\ddagger}\rangle + \langle u^{\ddagger}|Y^0(1s^{\dagger},1s^{\dagger})+Y^0(2s^{\dagger},2s^{\dagger})|u^{\ddagger}\rangle, \tag{84}$$

$$\epsilon(2s^{\dagger})=\langle v^{\dagger}|H_0|v^{\dagger}\rangle + \langle v^{\dagger}|Y^0(1s^{\dagger},1s^{\dagger})+Y^0(1s^{\ddagger},1s^{\ddagger})|v^{\dagger}\rangle- \langle v^{\dagger}|Y^0(1s^{\dagger},2s^{\dagger})|v^{\dagger}\rangle. \tag{85}$$

When we expand in powers of Z^{-1}, the corresponding zero-order equations are

$$\left.\begin{aligned}(H_0 - \epsilon_0(1s^{\dagger}))u_0^{\dagger} &= 0,\\ (H_0 - \epsilon_0(1s^{\ddagger}))u_0^{\ddagger} &= 0,\\ (H_0 - \epsilon_0(2s^{\dagger}))v_0^{\dagger} &= 0,\end{aligned}\right\} \tag{86}$$

which have the hydrogenic solutions

$$\left.\begin{aligned}u_0^{\dagger} = u_0^{\ddagger} = u_0 = 2\exp(-r),\quad & \epsilon_0(1s^{\dagger}) = \epsilon_0(1s^{\ddagger}) = \epsilon_0(1s) = -\tfrac{1}{2},\\ v_0^{\dagger} = v_0 = (1/2\sqrt{2})(2-r)\exp(-\tfrac{1}{2}r),\quad & \epsilon_0(2s^{\dagger}) = \epsilon_0(2s) = -\tfrac{1}{8}.\end{aligned}\right\} \tag{87}$$

Because of the identities of (87), the first-order equations are

$$(H_0-\epsilon_0(1s))u_1^{\dagger} + [Y_1^0(1s,1s)+Y_1^0(2s,2s) - \epsilon_1(1s^{\dagger})]u_0 = Y_1^0(1s,2s)v_0, \tag{88}$$

$$(H_0-\epsilon_0(1s))u_1^{\ddagger} + [Y_1^0(1s,1s)+Y_1^0(2s,2s)-\epsilon_1(1s^{\ddagger})]u_0 = 0 \tag{89}$$

and $$(H_0-\epsilon_0(2s))v_1^{\dagger} + [2Y_1^0(1s,1s)-\epsilon_1(2s^{\dagger})]v_0 = Y_1^0(1s,2s)u_0, \tag{90}$$

so that

$$\epsilon_1(1s^{\dagger}) = \left\langle u_0\middle|Y_1^0(1s,1s)\middle|u_0\right\rangle + \left\langle u_0\middle|Y_1^0(2s,2s)\middle|u_0\right\rangle - \left\langle u_0\middle|Y_1^0(1s,2s)\middle|v_0\right\rangle , \tag{91}$$

$$\epsilon_1(1s^{\ddagger}) = \left\langle u_0\middle|Y_1^0(1s,1s)\middle|u_0\right\rangle + \left\langle u_0\middle|Y_1^0(2s,2s)\middle|u_0\right\rangle , \tag{92}$$

$$\epsilon_1(2s^{\dagger}) = 2\left\langle v_0\middle|Y_1^0(1s,1s)\middle|u_0\right\rangle - \left\langle v_0\middle|Y_1^0(1s,2s)\middle|u_0\right\rangle . \tag{93}$$

The appropriate generalization of (21) for the total energies $E_n^{\dagger}$ is

$$\epsilon_n(1s^{\dagger}) + \epsilon_n(1s^{\ddagger}) + \epsilon_n(2s^{\dagger}) = (n+1)E_n^{\dagger} \tag{94}$$

from which it follows that

$$E_0^{\dagger} = E_0, \quad E_1^{\dagger} = E_1, \tag{95}$$

differences in the total energies derived from the restricted and unrestricted Hartree-Fock approximation appearing first in second order.

The second-order equations yield

$$E_2^{\dagger} = \left\langle u_0\middle|Y_1^0(1s,1s)\middle|u_1^{\dagger}\right\rangle + \left\langle u_0\middle|Y_1^0(1s,1s)\middle|u_1^{\ddagger}\right\rangle + \left\langle u_0\middle|Y_1^0(2s,2s)\middle|u_1^{\dagger}\right\rangle + \left\langle u_0\middle|Y_1^0(2s,2s)\middle|u_1^{\ddagger}\right\rangle$$
$$+2\left\langle v_0\middle|Y_1^0(1s,1s)v_1^{\dagger}\right\rangle - \left\langle u_0\middle|Y_1^0(1s,2s)\middle|v_1^{\dagger}\right\rangle - \left\langle v_0\middle|Y_1^0(1s,2s)\middle|u_1^{\dagger}\right\rangle . \tag{96}$$

The difference between the second-order energies derived from the unrestricted and restricted schemes may then be written

$$E_2^{\dagger} - E_2 = \left\langle \Delta u_1 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle \tag{97}$$

where Δu_1 is the function defined by

$$\Delta u_1 = u_1^{\ddagger} - u_1 \tag{98}$$

(cf. appendix II). With the use of the solution for Δu_1 derived in appendix III, it follows that

$$\begin{aligned} E_2^{\dagger} - E_2 &= - \frac{128}{531\ 441} \ \ln(9/8) - \frac{3\ 727\ 443\ 404\ 983}{1\ 594\ 323.10^{10}} \\ &= - 0{\cdot}00\ 026\ 216.... \end{aligned} \tag{99}$$

The small difference between the restricted and unrestricted eigenvalues is in harmony with the several variational calculations (cf. Nesbet 1960).

After these calculations were completed, a paper by Sharma (1962) appeared in which $E_2^{\dagger}$ was evaluated directly. Taken in conjunction with the restricted Hartree-Fock calculations of Linderberg (1961), Sharma's results are identical to (99).

Not only is the energy unchanged to first-order by relaxing the requirement that the 1s orbitals be identical but also the expectation value of any operator of the form (23). Thus the zero-order term of

$$\langle L \rangle^{\dagger} = (u^{\dagger}, \ell u^{\dagger}) + (u^{\ddagger}, \ell u^{\ddagger}) + (v^{\dagger}, \ell v^{\dagger}) \tag{100}$$

is identical to (25) and the first-order term is

$$\langle L \rangle_1^{\dagger} = \langle \ell | 1s^{\dagger} \rangle_1 + \langle \ell | 1s^{\ddagger} \rangle_1 + \langle \ell | 2s^{\dagger} \rangle_1; \tag{101}$$

the individual first-order contributions may be written, using (27) and (28),

$$\langle \ell | 1s^{\dagger} \rangle_1 = 2\langle x | Y_1^0(1s,1s) + Y_1^0(2s,2s) | u_0 \rangle - 2\langle x | Y_1^0(1s,2s) | v_0 \rangle, \tag{102}$$

$$\langle \ell | 1s^{\ddagger} \rangle_1 = 2\langle x | Y_1^0(1s,1s) + Y_1^0(2s,2s) | u_0 \rangle, \tag{103}$$

$$\langle \ell | 2s^{\dagger} \rangle_1 = 2\langle y | 2Y_1^0(1s,1s) v_0 \rangle - 2\langle y | Y_1^0(1s,2s) | u_0 \rangle, \tag{104}$$

and their sum is

$$\langle L \rangle_1^{\dagger} = 2\{\langle x | 2Y_1^0(1s,1s) + 2Y_1^0(2s,2s) | u_0 \rangle - \langle x | Y_1^0(1s,2s) | v_0 \rangle + \langle y | 2Y_1^0(1s,1s) | v_0 \rangle - \langle y | Y_1^0(1s,2s) | u_0 \rangle\}, \tag{105}$$

which is identical to (33).

3.2. The spin-density

The spin-density operator, which has attracted considerable attention in recent years (cf. Sharma 1962), does not have the form (23) and there occurs a difference in first order between the values predicted by the restricted and unrestricted approximations. The spin density is directly related to the quantity

$$\langle f \rangle = 4\pi\{\langle u^{\dagger} | \delta(r) | u^{\dagger} \rangle - \langle u^{\ddagger} | \delta(r) | u^{\ddagger} \rangle + \langle v^{\dagger} | \delta(r) | v^{\dagger} \rangle\}, \tag{106}$$

which reduces to

$$\left\langle f \right\rangle = 4\pi \left\langle v \middle| \delta(r) \middle| v \right\rangle \tag{107}$$

in the restricted approximation. From Table 2, (107) is given correct to first-order in Z^{-1} by

$$\left\langle f \right\rangle = \tfrac{1}{2}(Z - 1.0603)^3. \tag{108}$$

For lithium, (108) has the value 3.649, whereas the value computed from numerical Hartree-Fock orbitals is 2.095 (cf. Nesbet 1960).

Sharma (1962) has calculated (106) correct to first order by solving for $u_1^\dagger$, $u_1^\ddagger$ and $v_1^\dagger$. He obtains the result

$$\left\langle f \right\rangle = Z^3\left[\left(2 - \frac{0.648\ 795}{Z}\right)^2 - \left(2 - \frac{0.730\ 608}{Z}\right)^2 + \left(0.707\ 107 - \frac{1.170\ 325}{Z}\right)^2\right] \tag{109}$$

which for lithium has a value of 5.320. However, this procedure is not strictly a consistent one since (109) omits second-order terms arising from $\left\langle u_2^\dagger \middle| \pi\delta(r) \middle| u_0 \right\rangle$ while retaining $\left\langle u_1^\dagger \middle| \pi\delta(r) \middle| u_1^\dagger \right\rangle$.

The calculation can be carried out to a similar accuracy without determining $u_1^\dagger$, $u_1^\ddagger$, and $v_1^\dagger$. Thus it is easily shown that to first order

$$\left\langle f \right\rangle = 4\{ \left\langle v_0 \middle| \pi\delta(r) \middle| v_0 \right\rangle - 2\left\langle x \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle + 4\left\langle y \middle| Y_1^0(1s,1s) \middle| v_0 \right\rangle - 2\left\langle y \middle| Y_1^0(1s,2s) \middle| u_0 \right\rangle \}, \tag{110}$$

where x and y are the solutions of respectively (27) and (29) corresponding to $\ell = \delta(r)$. Evaluating (110), we obtain for the unrestricted approximation

$$\left\langle f \right\rangle = \tfrac{1}{2}Z^3 - \frac{1}{2187}(5024 - 2172\ln 3 + 384\ln 2)Z^2 + O(Z) \tag{111}$$

which becomes on application of the screening approximation

$$\langle f \rangle = \tfrac{1}{2}(Z - 0.8852)^3. \tag{112}$$

For lithium, (112) has the value 4.729. If we assume that (112) overestimates by the same factor as does (108), we obtain a modified value 2.715 for $\langle f \rangle$, which is close to that expected from a complete calculation with the unrestricted Hartree-Fock approximation. (The observed hyperfine splitting corresponds to a value of 2.9062 for $\langle f \rangle$).

It may be concluded that the Z-expansion procedure provides a quantitatively valuable method for rapidly assessing the consequences of relaxing the restrictions which are contained in the conventional Hartree-Fock approximation.

This work has been supported in part by N. A. S. A. and in part by a grant from the National Science Foundation.

APPENDIX I. VALUES OF THE SLATER INTEGRALS

$$\left\langle u_0 \middle| Y_1^0(1s,1s) \middle| u_0 \right\rangle = \frac{5}{8}, \tag{I1}$$

$$\left\langle u_0 \middle| Y_1^0(2s,2s) \middle| u_0 \right\rangle = \left\langle v_0 \middle| Y_1^0(1s,1s) v_0 \right\rangle = \frac{17}{81}, \tag{I2}$$

$$\left\langle u_0 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle = \frac{16}{729}, \tag{I3}$$

$$\left\langle u_0 \middle| Y_1^0(2s,2s) \middle| v_0 \right\rangle = \left\langle v_0 \middle| Y_1^0(1s,2s) \middle| v_0 \right\rangle = \frac{512\sqrt{2}}{3^3 \cdot 5^5}, \tag{I4}$$

$$\left\langle u_0 \middle| Y_1^0(2p,2p) \middle| u_0 \right\rangle = \left\langle w_0 \middle| Y_1^0(1s,1s) \middle| w_0 \right\rangle = \frac{59}{243} \tag{I5}$$

$$\left\langle u_0 \middle| Y_1^0(1s,2p) \middle| w_0 \right\rangle = \frac{112}{2187}. \tag{I6}$$

APPENDIX II. DERIVATION OF EQUATION (102)

The solutions of equations (12), (13) may be written formally

$$u_1 = u_0\{f_1(1s,1s) + f_1(2s,2s) - \tfrac{1}{2}f_1(1s,2s)\} + \tfrac{4}{3}\epsilon_1(1s,2s)v_0 \tag{II1}$$

and

$$v_1 = v_0\{2g_1(1s,1s) - g_1(1s,2s)\} - \tfrac{8}{3}\epsilon_1(1s,2s)u_0, \tag{II2}$$

where

$$(H_0 - \epsilon_0(1s))[u_0 f_1(\ell s,\ell s)] + \{Y_1^0(\ell s,\ell s) - \left\langle u_0\middle|Y_1^0(\ell s,\ell s)\middle|u_0\right\rangle\}u_0 = (\ell=1,2) \tag{II3}$$

and

$$(H_0 - \epsilon_0(1s))[u_0 f_1(1s,2s)] + \{Y_1^0(1s,2s)v_0 - \left\langle u_0\middle|Y_1^0(1s,2s)\middle|v_0\right\rangle u_0\} = 0, \tag{II4}$$

with similar equations for the g_1 functions.

Similarly, the solutions of (90), (91) and (92) may be written

$$u_1^{\dagger} = u_0\{f_1(1s,1s) + f_1(2s,2s) - f_1(1s,2s)\}, \tag{II5}$$

$$u_1^{\ddagger} = u_0\{f_1(1s,1s) + f(2s,2s)\}, \tag{II6}$$

and

$$v_1^{\dagger} = v_0\{2g_1(1s,1s) - g_1(1s,2s)\}. \tag{II7}$$

When the difference $(E - E_2)$ is written in terms of u_0, v_0 and the f_1, g_1 the result is

$$E_2^{\dagger} - E_2 = \tfrac{1}{2}\{\left\langle u_0 f_1(1s,2s)\middle|Y_1^0(1s,2s)\middle|v_0\right\rangle + \tfrac{8}{3}\left\langle v_0\middle|Y_1^0(1s,2s)\middle|v_0\right\rangle^2\} \tag{II8}$$

$$= \left\langle \Delta u_1\middle|Y_1^0)1s,2s)\middle|v_0\right\rangle \tag{II9}$$

from the definition of Δu_1 and the use of equation (16).

APPENDIX III. SOLUTIONS OF THE FIRST-ORDER EQUATIONS

We take as an example the equation (II4) for $f_1(1s,2s)$ which occurs in Δu_1 (equation (98) of the text):

$$(H_0 - \epsilon_0(1s))[u_0 f_1(1s,2s)] + \{Y_1^0(1s,2s)v_0 - \langle u_0|Y_1^0(1s,2s)|v_0\rangle u_0\} = 0. \tag{III1}$$

The equation for f_1 may be written

$$\mathscr{H}(u_0)f_1 + \frac{1}{u_0} Y_1^0 v_0 - \langle u_0|Y_1^0|v_0\rangle = 0, \tag{III2}$$

where

$$\mathscr{H}(u_0) = -\frac{1}{2}\left\{\frac{d^2}{dr^2} + 2\left(\frac{1}{u_0}\frac{du_0}{dr} + \frac{1}{r}\right)\frac{d}{dr}\right\}. \tag{III3}$$

We thus have a first-order equation for df_1/dr which may be integrated directly; the final result is

$$f_1(r) = 2\int [ru_0(r)]^{-2}dr \int_0^r \{u_0 Y_1^0 v_0 - \langle u_0|Y_1^0|v_0\rangle u_0^2\} s^2 ds + \text{constant}; \tag{III4}$$

the constant must be chosen so that $\langle u_0|f_1|u_0\rangle = 0$.

The solution $f_1(1s,2s)$ is thus found to be

$$f_1(1s,2s) = \{(-\frac{8}{729}(1/r) + \frac{112}{6561} + \frac{16}{729}r) + \frac{16}{729}\phi_1(r) - \exp(-r)(-\frac{8}{729}(1/r) + \frac{8}{21} + \frac{2}{27}r + \frac{1}{27}r^2)\}, \tag{III5}$$

with

$$\Phi_1(r) = \int_0^r \frac{1}{s}\,[1 - \exp(-s)]ds + \Phi_1(0) \qquad \text{(III6)}$$

$$\Phi_1(0) = -\left(\frac{11}{18} + \ln\frac{3}{2}\right) \qquad \text{(III7)}$$

to satisfy the orthogonality condition.

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